Field Evaluation of the Treatment of DNAPL Using Emulsified Zero-Valent Iron (EZVI)

Tom Krug, Suzanne O'Hara, Mark Watling (Geosyntec Consultants)

Jacqueline Quinn (NASA – Kennedy Space Center, FL)

Nancy Ruiz (NFESC, Port Hueneme, CA)

Chunming Su and Robert Puls (USEPA, Ada, OK)

Geosyntec consultants

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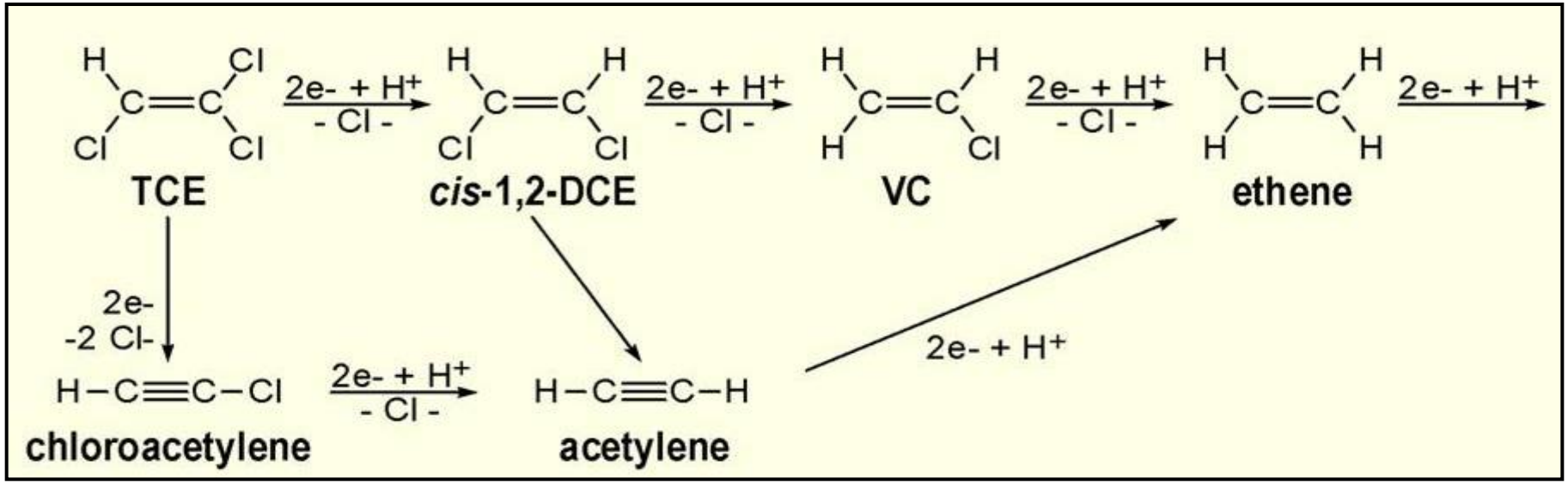
Outline

- EZVI Technology Background
- EZVI Applications
- ESTCP Project Objectives
- Overview of Lab Study
- Field Demonstration – Parris Island

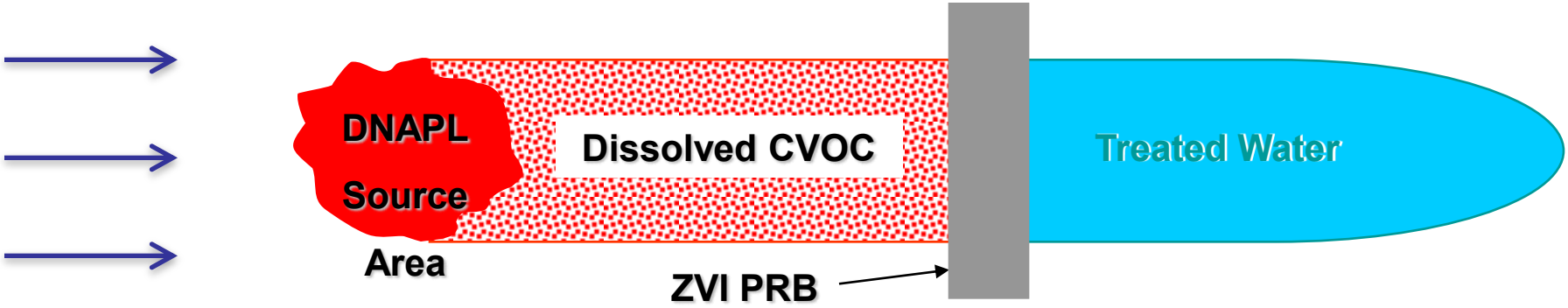
ZVI Chemistry

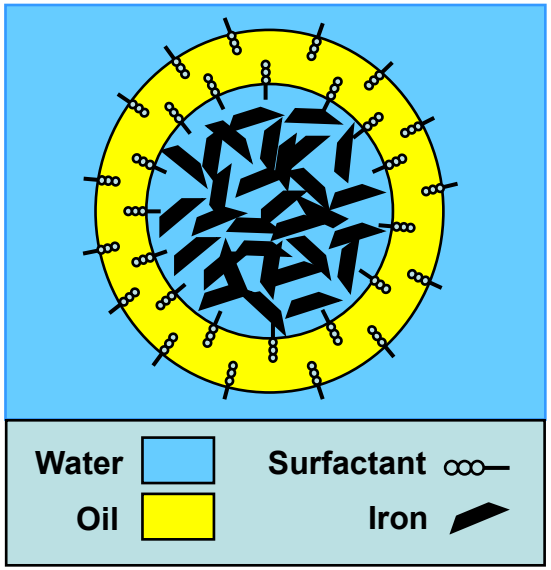
- ZVI is a strong reducing agent
- ZVI is an accepted technology for degradation of dissolved CVOCs such as PCE and TCE
- Basic chemistry the same for granular, micro- or nano-scale ZVI (mZVI or nZVI)

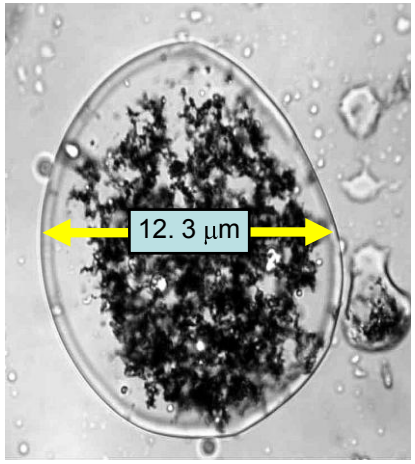


ZVI PRBs

- ZVI Permeable Reactive Barriers (PRBs) with granular iron are effective in treating dissolved CVOCs but:
  - are dependent on dissolution and transport of CVOCs
  - do little to reduce the clean up time and long-term monitoring costs
- ZVI needs to be in the presence of water to promote reductive dehalogenation
- Injection of ZVI into a DNAPL source zone will only treat the dissolved phase at the edges of the DNAPL







Properties of EZVI

- Emulsion droplets contain iron particles in water surrounded by an oil-liquid membrane
- Oil layer of emulsion is miscible with the DNAPL
- CVOCs diffuse through the oil membrane and are degraded by the ZVI
- EZVI enhances contact between the DNAPL and the ZVI particles
- Vegetable oil act as electron donor and promotes anaerobic biodegradation

Image of EZVI and DNAPL Contact

DNAPL
dyed red

DNAPL
with nano-scale ZVI

DNAPL
with EZVI

EZVI Technical Capabilities

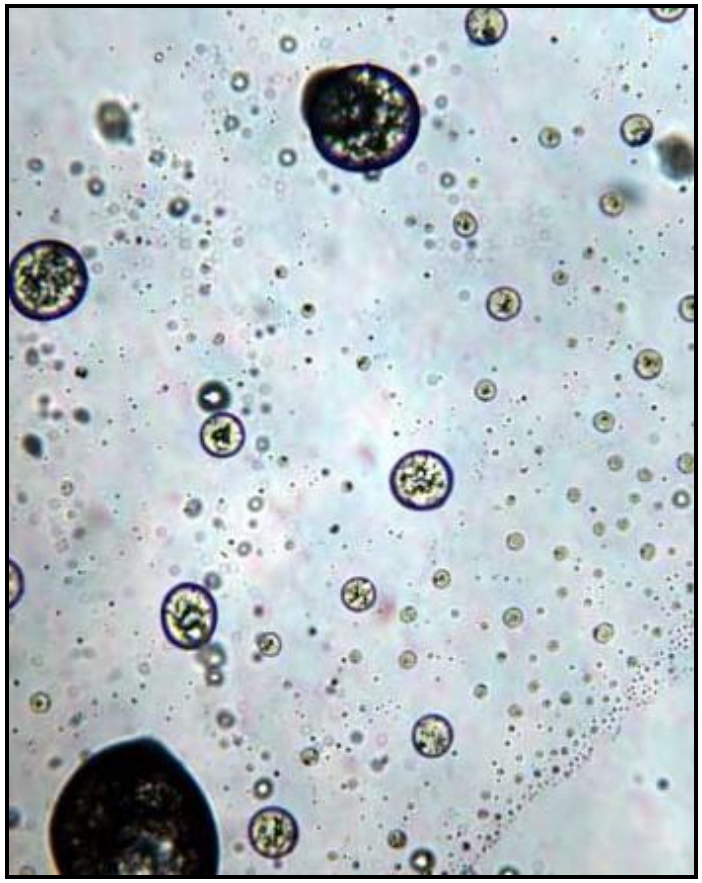
- Combines capabilities of three remediation technologies:
  - Zero-valent iron (ZVI) – abiotic degradation
  - Biodegradation - biodegradation
  - Oil sequestration – mobility reduction
- Enhances contact between ZVI and DNAPL

EZVI Application Methods

- Injection
  - Direct injection
  - Pneumatic injection
  - Pressure pulse injection
  - Hydraulic fracturing
- Large diameter auger mixing
- Viscous fluid can be difficult to emplace in the target treatment interval

Application History

- NASA holds the patent for EZVI
- Technology has been successfully commercialized by NASA and has been licensed to six companies
- EZVI awarded Invention of The Year and Commercial Invention of The Year by NASA and the Federal Government, and was inducted into the Space Technology Hall of Fame
- 16 Sites from 2002 - 2008



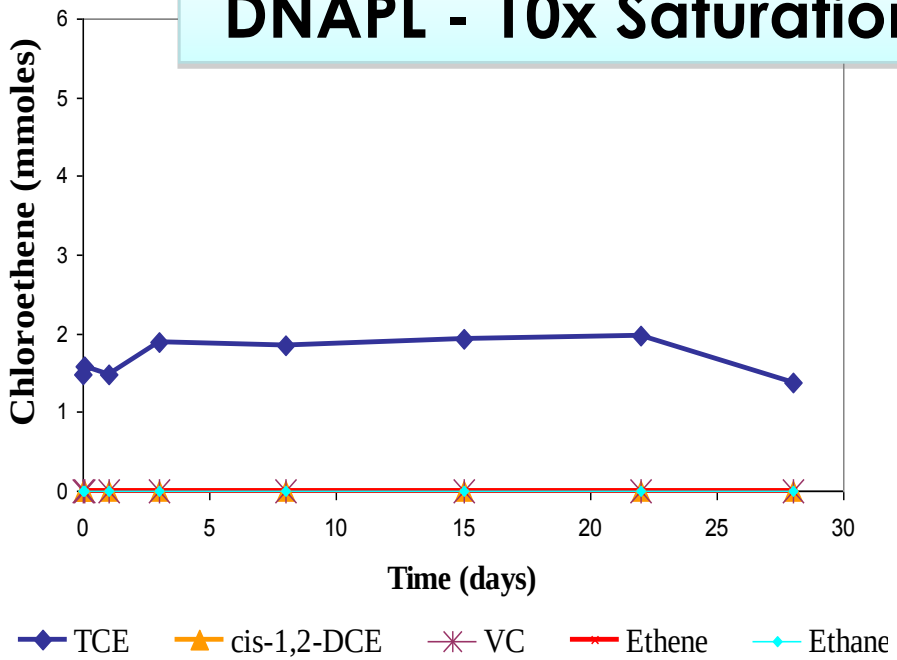
ESTCP Project Objectives

- **Laboratory Study:**
  - Evaluate degradation mechanisms - Completed 2005
- **Field Demonstration Testing:**
  - Inject EZVI into two pilot test areas within a DNAPL source zone using: Direct Injection, Pneumatic Injection
  - Evaluate ability of EZVI to reduce mass flux of CVOCs from a DNAPL source zone and reduce the DNAPL mass

Treatability Testing

- **Lab tests conducted to evaluate treatment of near saturation dissolved phase concentrations (1000 ppm) and DNAPL (10 x saturation) using:**
  - Controls (active and sterile)
  - Vegetable oil & surfactant (Emulsion)
  - nZVI
  - nZVI in EZVI
- **Monitor VOCs, DHG and chloride in the water phase of each reactor**

DNAPL - 10x Saturation (16.7 mmoles)



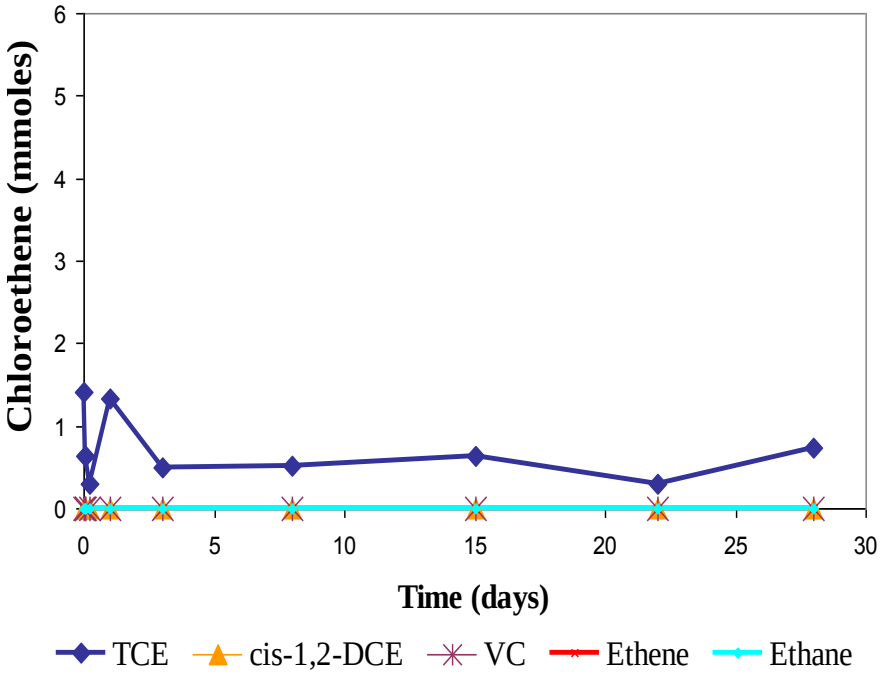
Active Control

CE at saturation concentration

o degradation by-products bserved (no DHG or chloride)

Oil Emulsion Treatment

- TCE stable at ~30% of saturation concentration
- No degradation by-products observed (no DHG or chloride)
- DNAPL sequestered in oil phase – equilibrium concentrations lower than for pure phase DNAPL



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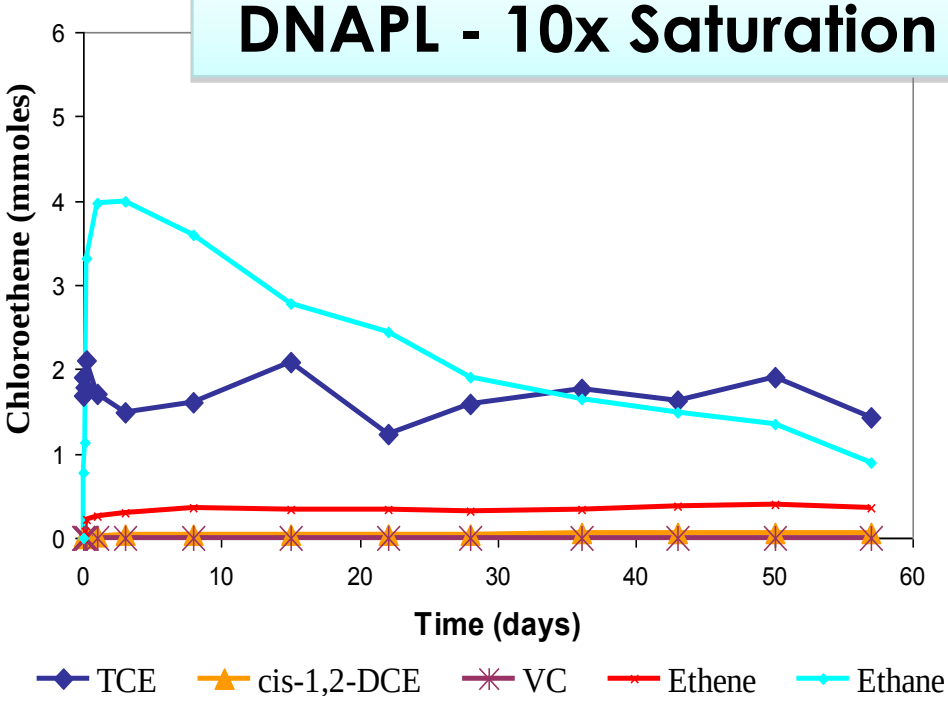
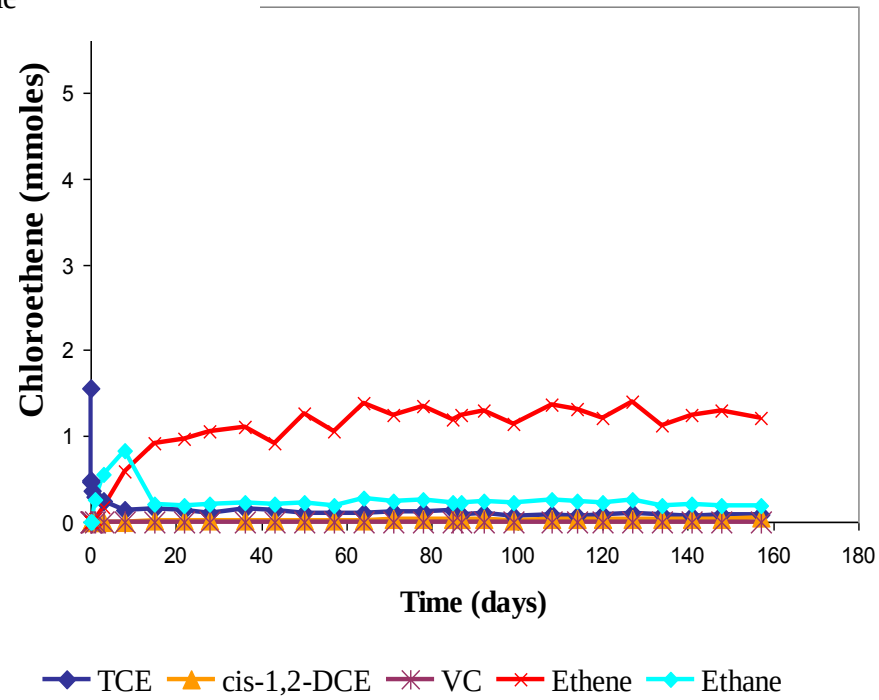


ZVI Treatment

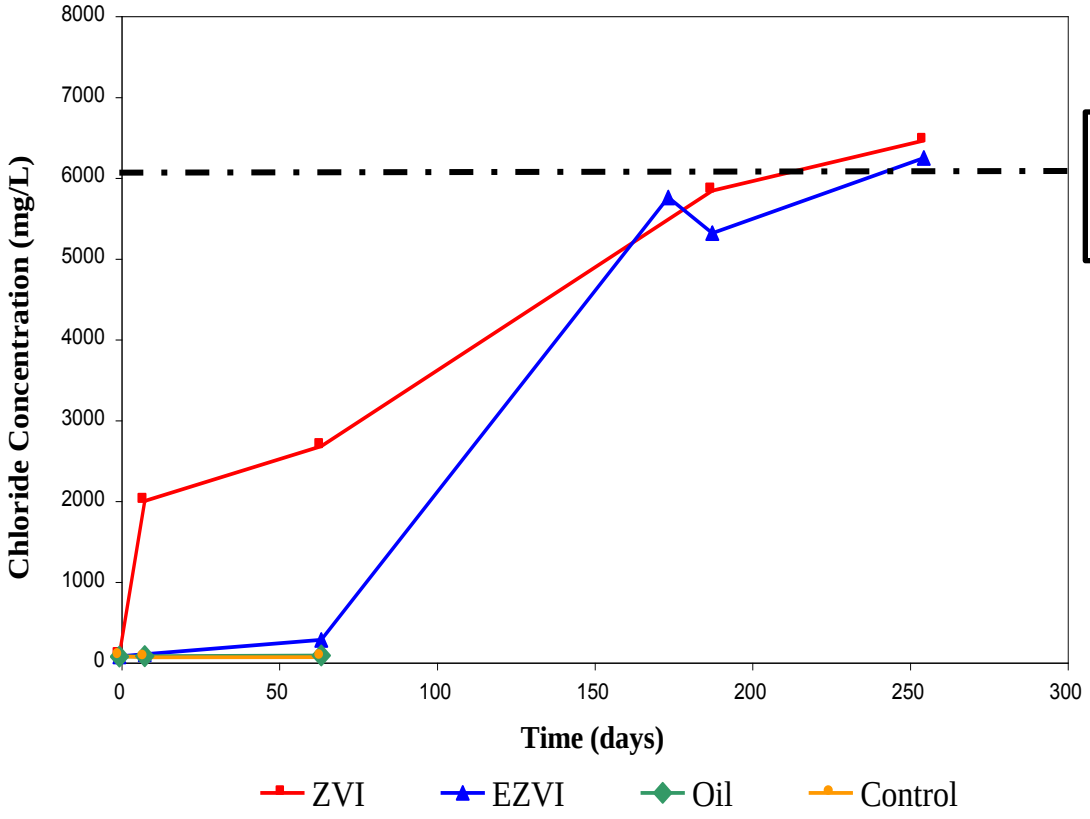
- stable at saturation
  entration
- adation by-products
  rved (ethane and ethene)
- ride production indicates
  adation of ~73% of TCE

EZVI Treatment

- TCE ~10% of saturation concentration and dropping
- Degradation by-products observed (ethane and ethene
- Chloride production indicates degradation of ~71% of TCE



EZVI Lab Testing – Chloride Production

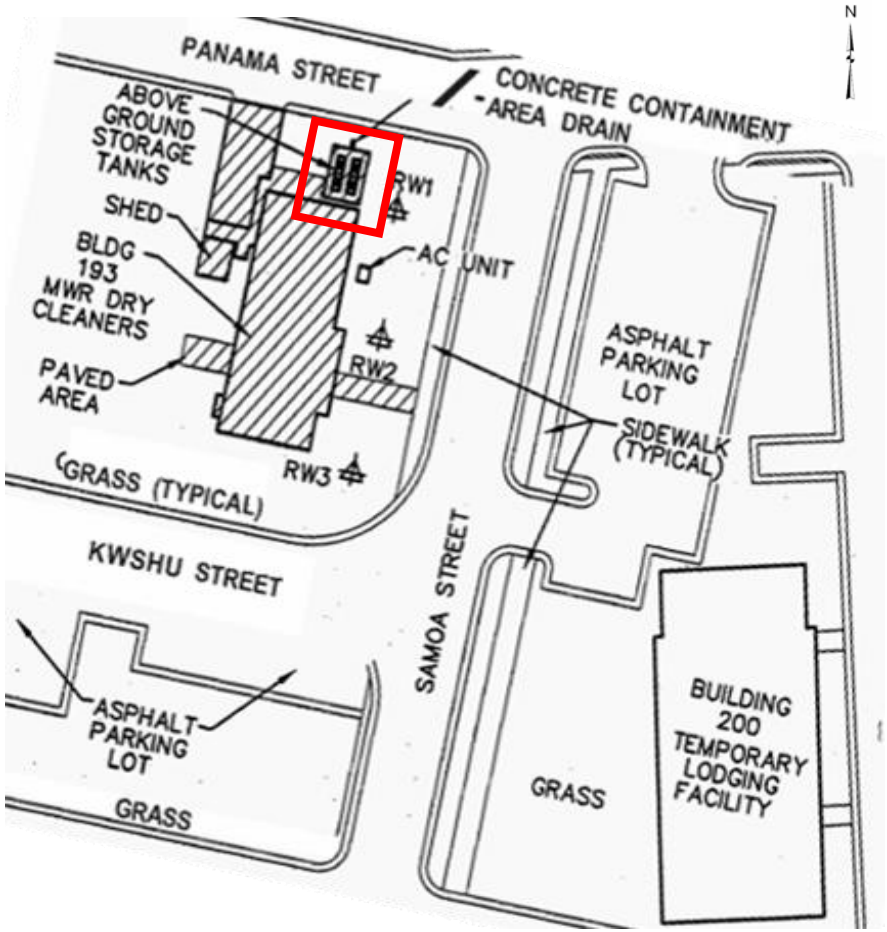


70% conversion of TCE to ethene

Conclusions – Lab Testing

- EZVI benefits from sequestration due to oil plus degradation due to nZVI
  - Significant decrease in aqueous concentrations (drop in mass flux) greater than with just the oil; and
  - Reduction in mass of TCE
- Impacts of biodegradation not significant in these tests which utilized synthetic groundwater and no soil (expect to see biodegradation with emulsion and EZVI)

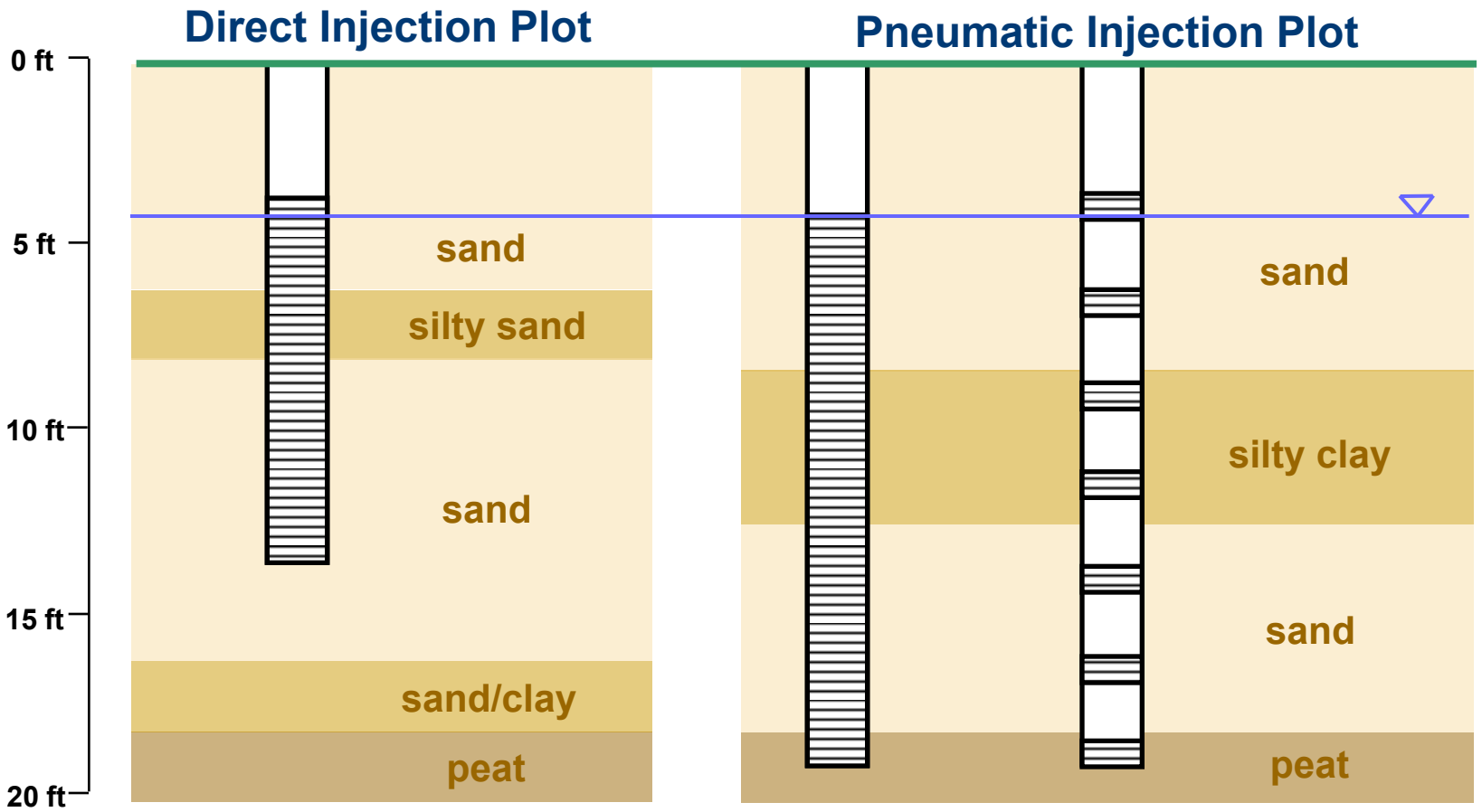
Case Study - Parris Island



- Environmental Securities Technology Certification Program (ESTCP) project ER-0431
- Site 45, Parris Island MCRD, SC
- Former dry cleaning facility
- Buildings have been torn down
- Source areas located around former above and below ground storage tanks

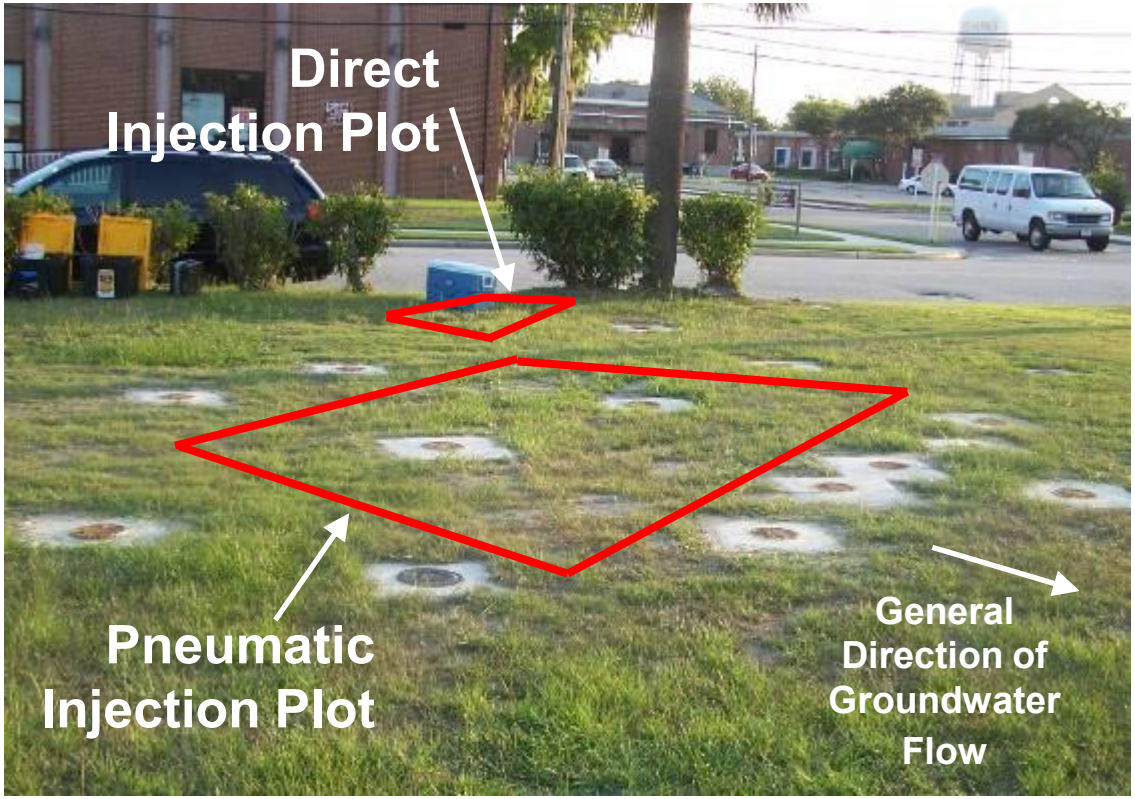
Demonstration Site

Fully screened and multilevel wells



Demonstration Site

Multilevel Well Construction



Direct and Pneumatic Injection Plots

EZVI Preparation

- EZVI prepared on-site by mixing nano-scale iron (Toda), corn oil, surfactant and water in drums using top mounted industrial mixer
- EZVI pumped from mixing drums into injection tanks





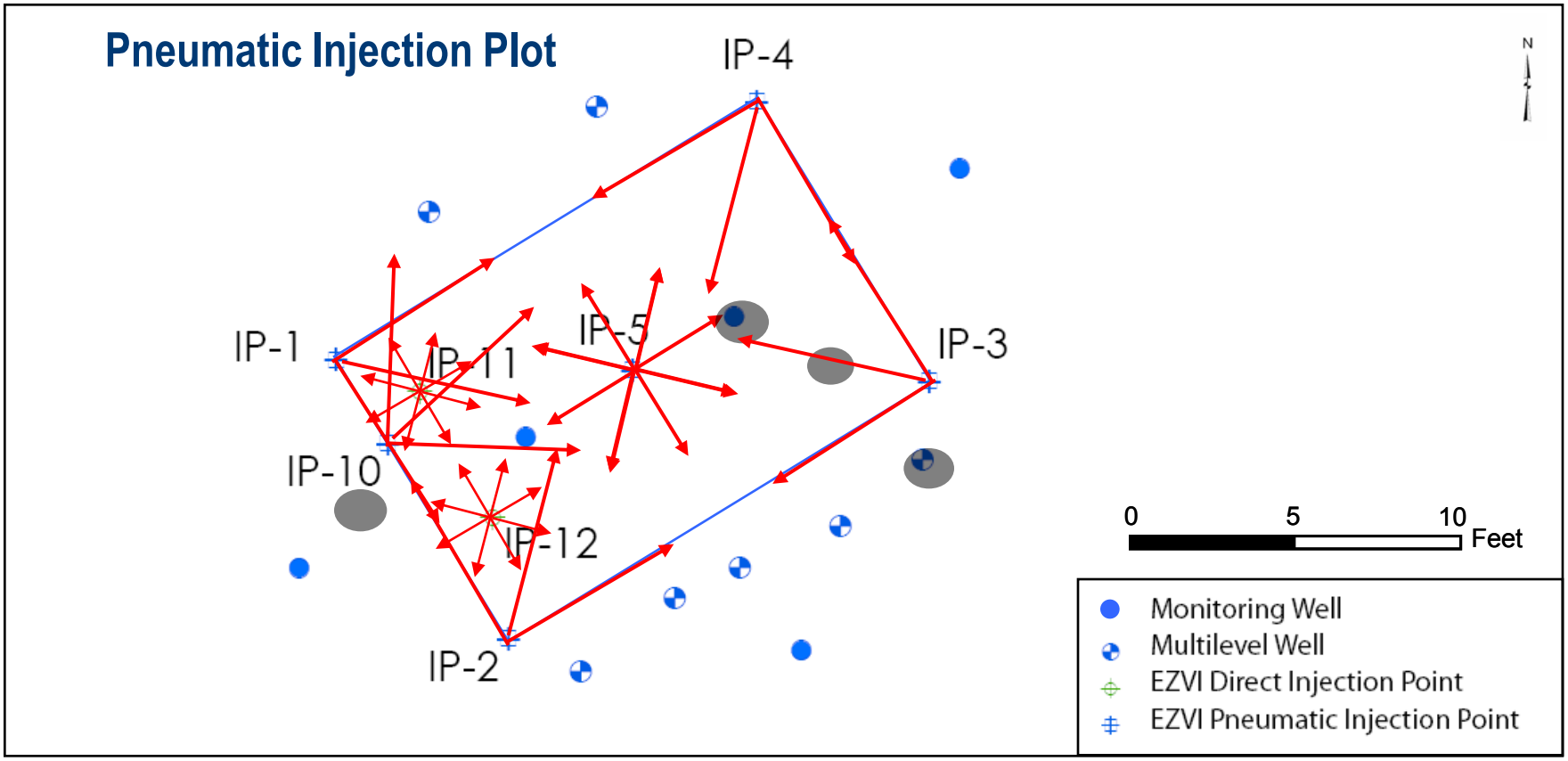


EZVI Injections

Pneumatic Injection Plot

- 575 gal EZVI injected into 8 locations between 7 and 19 ft bgs (2 locations using Direct Injection)
- During injections, monitored injection pressure, pressure distribution in subsurface, ground heave, and looked for EZVI at ground surface (daylighting)

Pneumatic Injection Plot



EZVI Injections

- EZVI daylighted in both Pneumatic and Direct Injection test plots

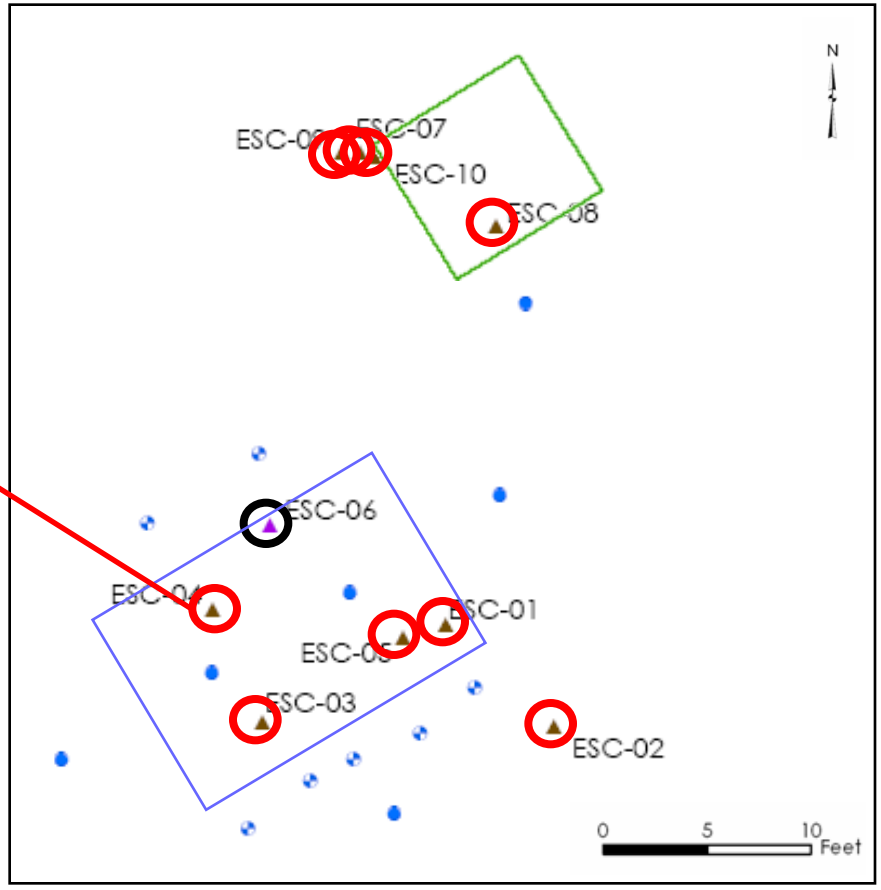
Pneumatic Injection plot (daylighting around ML-3 pad, downgradient of plot)

Direct Injection plot (daylighting possibly from old soil core location)

Soil Cores – Distribution

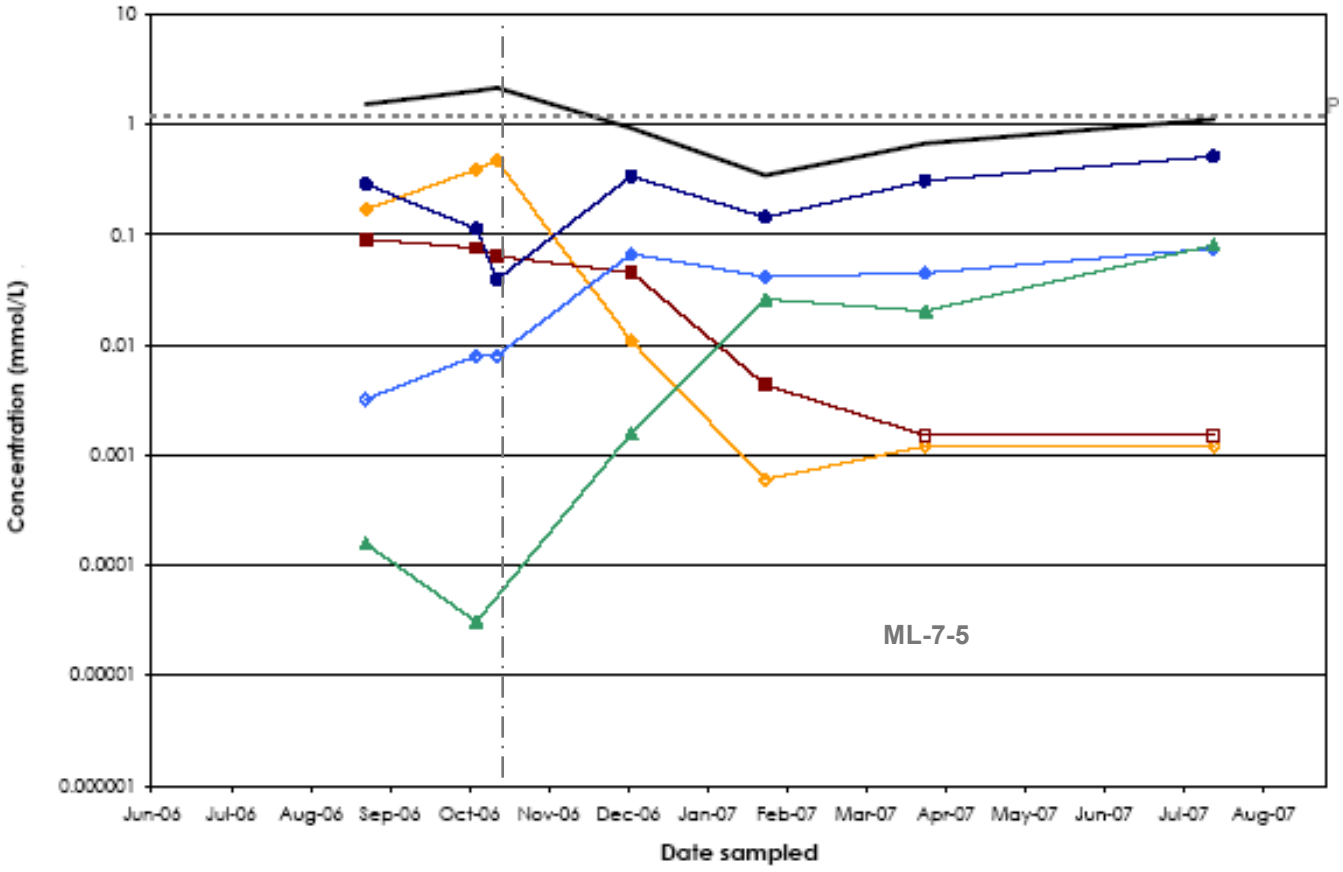
- Cores collected to evaluate ability of injection technologies to distribute EZVI evenly over target treatment intervals

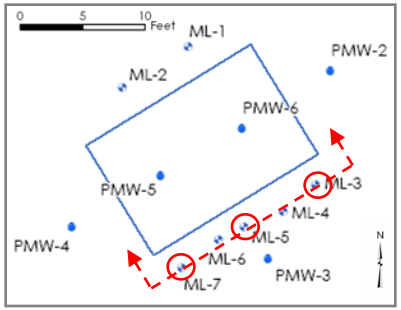
sand saturated with EZVI



- EZVI in all cores but one (ESC-06)

VOC Trends: Downgradient Well

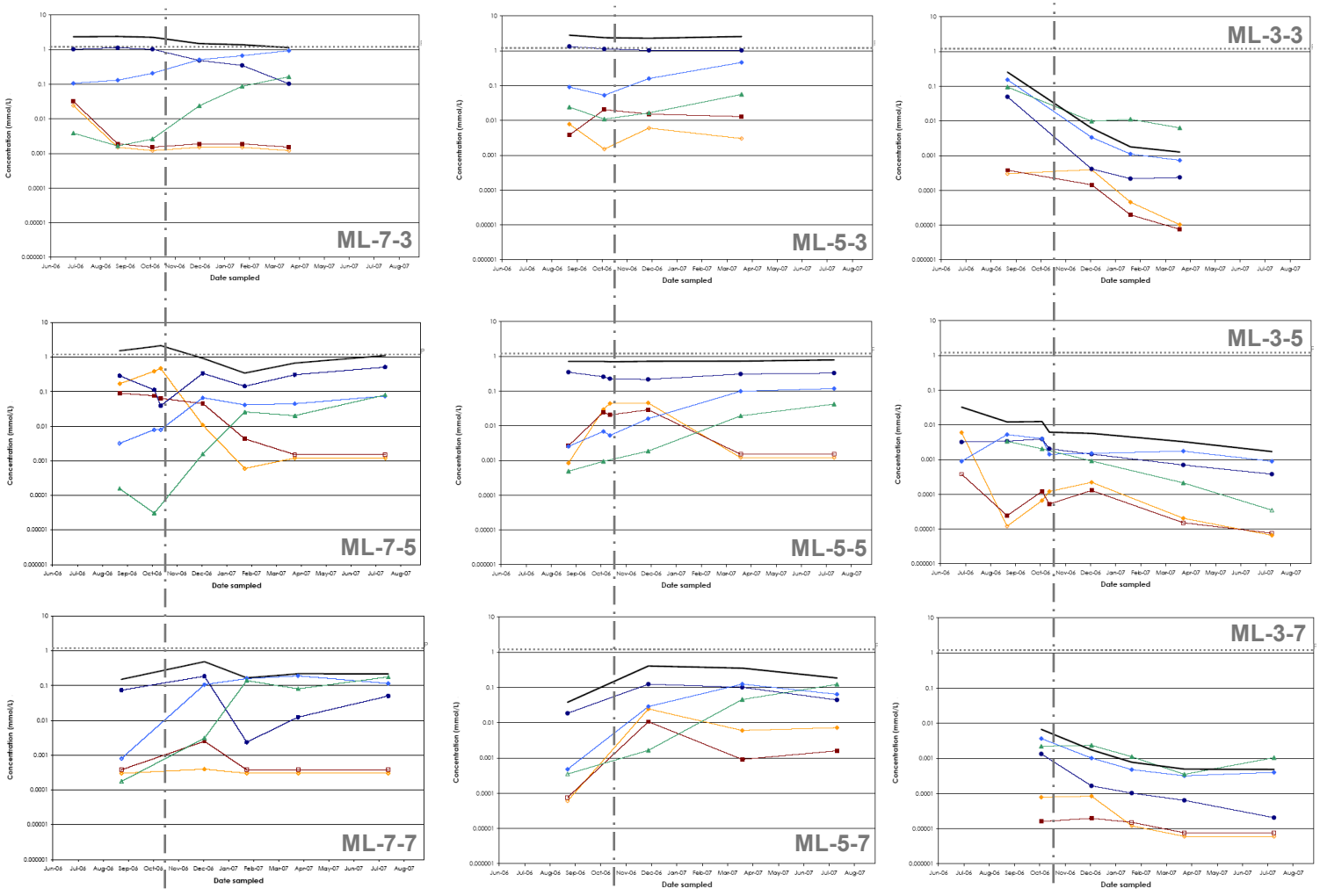


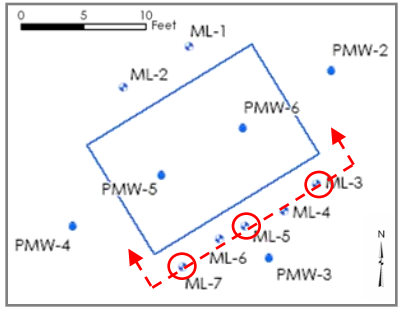


PCE
TCE
cDCE
VC
Ethene
Chlorine
PCE Solubility (200 mg/L; Pankow & Cherry)

EZVI Injections

VOC Trends: Downgradient wells in Pneumatic Injection Plot





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EZVI Injections

Summary of Case Study

- Downgradient wells show decrease in PCE/TCE with increase in degradation products including significant increases in ethene
- Upgradient wells and PMW-5 show continued presence of DNAPL although significant production of ethene in PMW-5 indicates that degradation is ongoing in the area
- DNAPL now being pumped from some wells where DNAPL was previously absent, indicating that some of the DNAPL is mobile
- Difficulty distributing EZVI due to shallow application and short-circuiting up existing investigation boreholes

Modified EZVI Applications

- mZVI versus nZVI to make EZVI
- Co-injection of ZVI and vegetable oil
- Bioaugmentation to enhance biodegradation
- Applications for co-mingled plumes or sources where either ZVI or bioremediation on its own wouldn't work

Acknowledgements

- Project funding provided by ESTCP (ER-0431)
- USEPA (GWERD, National Risk Management Research Laboratory) provided drill rig for soil cores and well installations. Also providing field sampling support, equipment and analytical support
- Pneumatic injections performed by Pneumatic Fracturing, Inc. (Alpha, NJ)
- Direct injections performed by Vironex, Inc. (Golden, CO)
- Tim Harrington, Parris Island MCRD

Supplemental Slides

Cost of EZVI

- Cost of nZVI and to lesser extent mZVI drives cost of EZVI
- Cost of other ingredients are minimal (up to $6/gal)
- Small volumes can be prepared on-site; larger volumes prepared and shipped to the site
- Costs for EZVI with nZVI significantly more than with mZVI:
  - ~$10/gallon with BASF mZVI
  - ~$28/gallon with Toda nZVI

Iron Product	Supplier	Cost
Nano-scale ZVI	Toda America	$26-$34 / lb
Micro-scale ZVI (40,000 nm)	Hepure (ARS)	$1.00 to $1.70/lb
Micro-scale ZVI (up to 3,000 nm)	BASF	$4.00 / lb
Granular Iron (comparison only, can't use to make EZVI)	Peerless Metal Products, Master Builders, QMP, Connelly	$0.40 / lb